

Comparison of Optical Properties of Bulk and Nano Crystalline Thin Films of CdS Using Different Precursors

Ruby Das^{#1}, Suman Pandey^{*2}

[#]Department of Applied Physics, Bhilai Institute of Technology,
Durg, Chhattisgarh Swami Vivekanand Technical University,

^{*}Department of Applied Physics, Rungta College of Engineering & Technology,
Bhilai, Swami Vivekanand Technical University,
¹dwijendrad@yahoo.co.in, ²sumu_74@rediffmail.com

Abstract-The optical properties of bulk as well as nano CdS thin films developed by the Chemical Bath Deposition (CBD) were investigated in this paper. Results of optical Transmission, absorption, reflection spectra, optical conductance, refractive index, extension coefficient, real and imaginary dielectric constants studies are reported. The optical properties were obtained using UV-VIS Double Beam Spectrophotometer Version 6.51 in the wavelength range 200-1100 nm. The optical transmittance of the film of nano CdS formed at 50°C was 99% at wavelength ≈ 475nm then decreases to 90% at wavelength ≈ 482nm for thin film of nano CdS at room temperature and 75% transmittance at wavelength ≈ 490nm for thin film of bulk CdS. The band-gap was also calculated from the equation relating absorption co-efficient with the wavelength. The energy band gap changes from 2.5eV (Bulk CdS) to 3.6eV (nano CdS at 50°C). The plotted graphs show the optical characteristics of the film which varied with the wavelength and the photon energy. The optical conductance and band-gap indicated that the film is transmitting within the visible range. The dielectric constant and optical conductance of the film initially increases slowly then abruptly and finally becomes constant with increase in photon energy. The extinction coefficient and refractive index of the films also evaluated, which affected with the change in transmittance. The dielectric constant changes with change in photon energy.

Keywords-Chemical bath deposition; transmittance; absorbance; reflectance; band-gap; dielectric constant; refractive index; extinction coefficient; CdS

I. INTRODUCTION

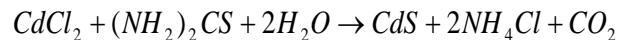
Currently there is a great deal of interest in optical and structural properties of nanometer sized semiconductor particle or thin films [1]. CdS has intermediate energy band gap, reasonable conversion efficiency, stability and low cost therefore it is one of the most widely used material for CdS/CdTe and CdS/Cu₂S heterojunction solar cells or device applications [2]. Nanocrystalline thin films of II-VI semiconductor have attracted particular attention, because they are relatively easy to synthesis in the size range required for quantum confinement. They are currently of great interest for their practical applications such as zero-dimensional quantum confined material, and in optoelectronics and photonics. Numerous reports are available in the literature on synthetic techniques as well as potential applications of nano-sized semiconductor particles [3]-[7]. They show significant

departures from bulk optical and structural properties when scale of confinement approaches to excitonic Bohr radius which sets the length scale for optical process [8]. CdS is a wide band gap semiconductor with E_g 2.4eV [9]. The optical properties of CdS have been extensively studied [10]. Reduction in particle size strongly influences the crystallinity of the film. The thickness of the film was observed about 34.8nm when film was annealed at 360°C for 1 hr [11]. CdS thin film have been fabricated using several deposition techniques such as screen printing [8], electro deposition [9], molecular beam epitaxy (MBE) [1], physical vapor deposition [10]. All these techniques require high sophisticated instrument and mismatch of thermal expansion coefficient between the film and substrate cause micro cracks. One of the promising techniques for producing large areas of inexpensive CdS film is chemical bath deposition and here we followed this method to synthesis the CdS films.

II. EXPERIMENTAL DETAILS

A. Preparation of Bulk CdS Thin Film

Bulk CdS thin films were prepared by Chemical Bath Deposition method from aqueous solution containing cadmium chloride (0.01M), zinc chloride (0.1M), thiourea (0.1M), 25% ammonia solution and triethanolamine (TEA) as a capping agent. The chemical bath is prepared from CdCl₂ solutions and 4% of the volume of the metal precursors, triethanolamine. The solution is stirred well for 5 minutes and required amount of ammonia solution (25% of NH₃ solution) was added to get a pH value 11. After proper stirring the solution with homogenizer for 10 minutes at the rate (125 rpm), thiourea is added into it and the reaction mixture was kept in a water bath at 50°C. Before the deposition of cadmium sulphide on glass slides, the slides (substrate) were degreased in hydrochloric acid (HCl) for 24 hours, cleaned in detergent/cold water, and then rinsed with distilled water and allowed to drip dry in air. The substrate immersed vertically in the chemical bath and the deposition was carried out for 60 minutes. After the deposition, the films were rinsed in distilled water and dried in open air at room temperature.



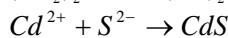
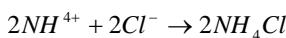
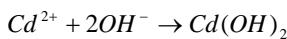
B. Preparation of Nano CdS Thin Films

1) Nano Cds Thin Film at Room Temperature

Nano CdS thin film was prepared from aqueous solution of cadmium sulfate (1M) as a source for cadmium, thiourea (1M) as the source of sulphur and NH₄OH solution. The Chemical bath is prepared from the solution of CdSO₄ and (NH₂)₂CS. The solution is stirred well for 5 minutes and required amount of NH₄OH is added to get pH of 10.25. The solution was stirred with homogenizer continuously at the rate (125 rpm). A cleaned glass substrate (were degreased in hydrochloric acid (HCl) for 24 hours, cleaned in detergent/cold water, and then rinsed with distilled water and allowed to drip dry in air) was immersed vertically in the chemical bath and the deposition was carried out for 60 minutes. After the deposition, the films were rinsed in distilled water and dried in open air at room temperature.

2) Nano CdS Thin Film at 500C Temperature

Nano CdS thin can also prepared with the same precursors with the same preparation method for 60 minutes deposition at different bath temperatures of 50°C, 60°C and 80°C but the best result obtained at 50°C with smooth, uniform thin film deposition was carried out.



Overall reaction:



III. RESULTS AND DISCUSSION

A. UV Spectral Studies

1) Optical Transmittance Spectra

The transmittance spectrum of samples is taken by UV-VIS Double Beam Spectrophotometer Version 6.51 in the wavelength range 200-1100 nm. The UV spectra of the material provide important information about the details related with optical band. Fig.1 shows the wavelength dependence transmittance of the films of bulk and nano material CdS in the wavelength range 300nm-900nm.

The optical transmittance of the film formed at 50°C was about 99% at wavelength 475nm then decreases to 90% transmittance at wavelength 482nm and of 75% transmittance at wavelength 490nm for thin film of bulk CdS. The optical transmittance increases from bulk to nano CdS thin film at 50°C. It is observed that the transmission spectra shift towards shorter wavelength as the particle size decreases which suggest the increase in optical energy band gap. It is supposed that the tightly adherent collides are formed with the change in micro to nano particle size.

The optical absorption coefficient (α) was evaluated by Tauc relation $\alpha h\nu = A(h\nu - E_g)^n$ $\alpha = 2.3026 \frac{A}{t}$, where A is constant called absorption coefficient, t is the film thickness, hν is the photon energy ($\nu = \frac{c}{\lambda}$, E_g is the band gap and n=1/2 for allowed direct transition.

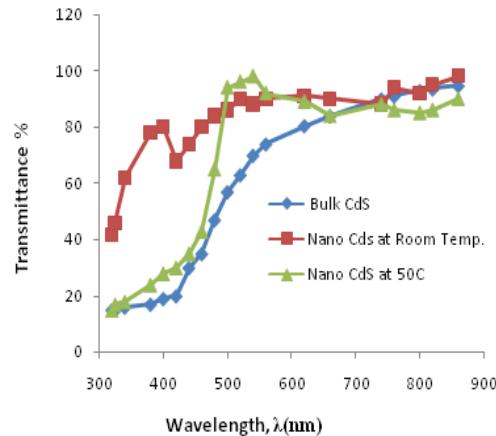


Fig.1. Transmittance Spectra of Bulk & nano CdS thin films

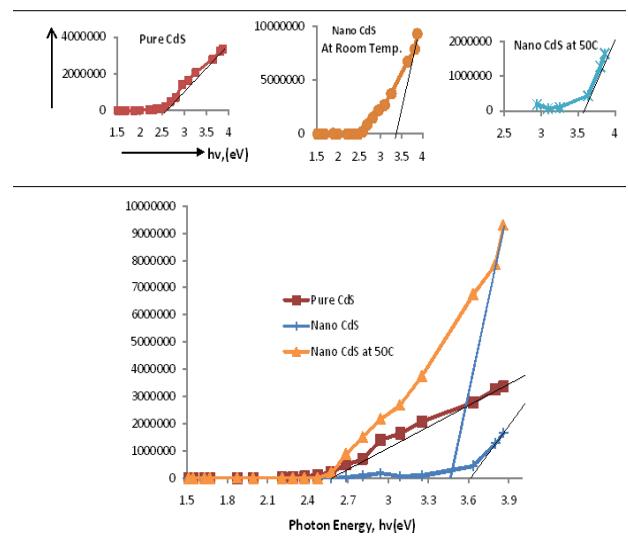


Fig.2 Plot between $(\alpha h\nu)^2$ and $h\nu$ for different deposition conditions for band gap measurement.

Plotting the graph between $(\alpha h\nu)^2$ versus photon energy ($h\nu$) gives the value of direct band gap. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$, gives the value of band gap, shown in Fig.2. From the UV spectra, it is clear that the absorbance decreases with increase in wavelength. This increase in transmittance indicates the presence of optical band gap in the material. The optical band gap of the films increases from 2.5eV to 3.6 eV from bulk to nano CdS thin films. The difference in the optical band values achieved was mainly due to the difference in the deposition techniques employed and the process parameter maintained during the growth of the films.

The band gap increases from bulk CdS to Nano CdS at 50°C. The highest blue shift energy is found to be 1.18eV. From the band gap information, the size of the CdS quantum dots were calculated using Effective Mass Approximation (EMA) method and Hyperbolic Band Model (HBM) using the following equations[12]:

$$E_{gn} - E_{gb} = \frac{\hbar^2 \pi^2}{2R^2 m^*}$$

and for HBM

$$E_{gn}^2 = [E_{gb}^2 + 2\hbar^2 E_{gb} (\pi/R)^2 / m^*]$$

In the above two equations, m^* is the effective mass of the specimen, E_{gb} is the bulk band gap and E_{gn} is the band gap of the sample.

2) Optical Absorbance Spectra

Optical absorbance against the wavelength is observed for CdS thin films in the wavelength range 300–900 nm with glass as the reference and is shown in Fig.3.

The ratio of radiant power transmitted (P) by a sample to the radiant power incident (P_0) on the sample is called the transmittance T:

$$T = \frac{P}{P_0}$$

$$\text{But, } P = P_0 e^{-\alpha t}$$

Where t is the thickness and $\alpha = (h\nu - E_g)^{1/2}$

$$\text{We have } T = e^{-\alpha t} \text{ or } \alpha = 2.303 \frac{A}{t}$$

Therefore using the fundamental relation of photon transmission and absorbance the Absorbance (A) is defined as the logarithm (base 10) of the reciprocal of the transmittance.

$$A = \log_{10} \frac{1}{T} \text{ or } A = -\log_{10} T = -\log_{10} \frac{P}{P_0}$$

The absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge of the

threshold wavelength for onset of absorption, the energy corresponding to this determines the band gap of the semiconductor material. The CdS film shows absorption coefficient (α) of about $1.4 \times 10^{-6} \text{ m}^{-1}$ near the absorption edge of wavelength 600 nm for bulk CdS, 1.48×10^{-6} for nano CdS thin film near the edge of wavelength 500 nm at room temperature and 2.5×10^{-5} for nano CdS thin film near the edge of wavelength 420 nm at 50°C. This shows that the deposited semiconductor films have a direct band gap material. It is observed that the absorption edge shifts towards shorter wavelength from bulk CdS thin film to nano CdS thin film at 50°C. The absorption onset in CdS-PVK thin film obtained at 300nm, gives band gap of 4.13eV [13].

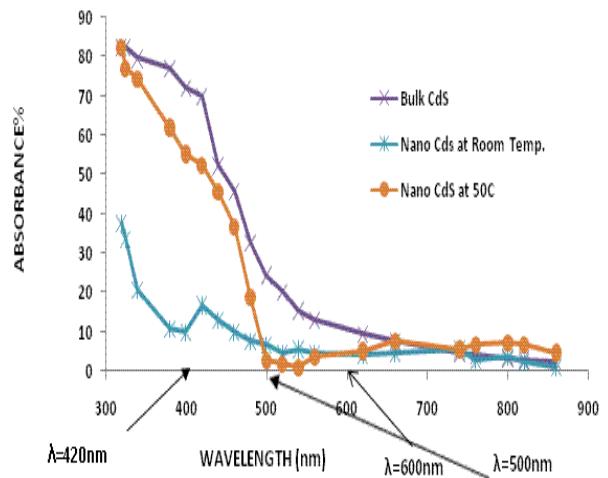


Fig.3. Absorption Spectra of Bulk & nano CdS Thin films

3) Optical Reflectance Spectra

If T is the Transmittance and A is the absorbance of the film then, the reflectance of the film has been found by using relationship.

$$R + T + A = 1 \text{ or } R = 1 - (T + A)$$

The reflectance of the bulk thin film initially increases with increase in wavelength up to 500nm after that it decreases up to 900nm due to increase in transmittance.

TableI VARIATION OF SIZE WITH DIFFERENT COMPOSITIONS FOR 60 MIN. DEPOSITIONS

Composition	λ (nm)	Band Gap, E_g (eV)	Blue Shift Energy(eV)	Transmittance (T%)	EMA(nm)	HBM(nm)
Bulk CdS	490 nm	2.5	0.08	75%	9.72 nm	13.6 nm
Nano CdS	482 nm	3.2	0.78	90%	2.77 nm	3.5 nm
Nano CdS at 50C	475 nm	3.6	1.18	100%	2.53 nm	3.2 nm

The nano CdS thin film at room temp decreases up to 400nm then increases abruptly of 15% and after that it decreases with increase in wavelength. The reflectance of the nano CdS at 50°C initially increases up to 480nm after that it decreases abruptly up to 530nm then increases slowly with increasing wavelength up to 650nm then again decreases and shows parabolic path up to 900nm because of change in transmittance. The reflectance is high (20%) in near infrared and visible region shown in Fig.4.

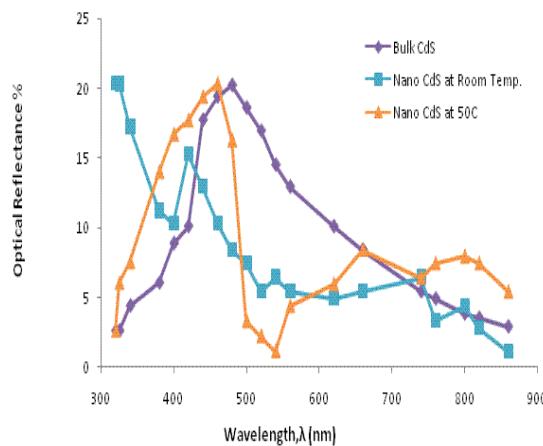


Fig.4 Reflectance Spectra of Bulk & nano CdS Thin films

B. Optical Conductance

The optical conductance is obtained using the relation,

$$\sigma = \alpha n c \epsilon_0 \quad \text{or} \quad \sigma = \frac{\alpha n c}{4\pi}$$

Where σ is the optical conductance, c is the velocity of the radiation in the space; n is the refractive index and α is the absorption coefficient.

Fig.5 shows the variation of optical conductivity with the incident photon energy. The increased optical conductivity at high photon energies is due to high absorbance of CdS film in that region. The optical conductance and band gap indicated that the film is transmittance within the visible range [14].

The conductivity is constant up to 2eV of photon energy after that it increases with increase in photon energy. This shows that when the absorption of photon by film increases in that region. The conductivity peak of the films increases from bulk to nano CdS thin films.

C. Refractive Index

The refractive of the film has been calculated by knowing reflectance that can be determine by formula [15]:

$$R = \frac{(n-1)^2}{(n+1)^2}$$

Where, R is the normal reflectance.

Using this relation refractive index n can be determined by the formula:

$$n = \frac{[(R^{1/2}) - 1]}{[(R^{1/2}) + 1]}$$

Fig.6 shows the variation in the refractive index with the incident photon energy. The refractive index of the bulk CdS thin film initially increases with increase in photon energy up to 2.6eV after that it decreases with increase in photon energy due to increase in reflectance. The refractive index of nano CdS thin film deposited at room temperature increases exponentially with increase in photon energy where as the refractive index of the nano CdS thin film deposited at 50°C initially decreases then increases and finally decreases with increase in photon energy due to change in reflectance of the film.

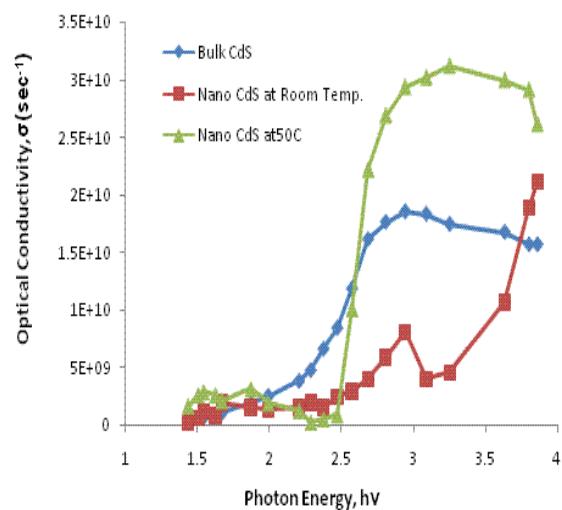


Fig.5 Optical Conductivity of Bulk & nano CdS Thin films

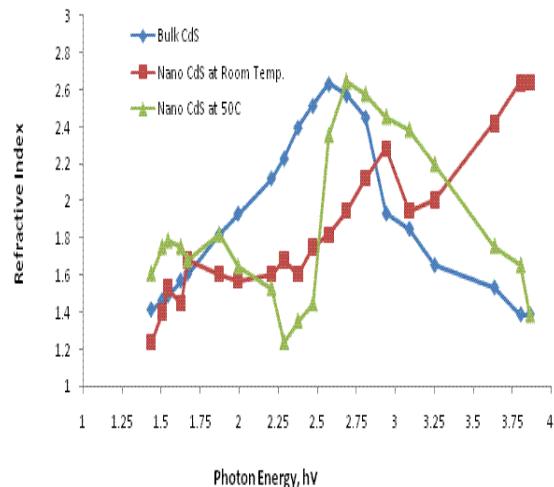


Fig.6 Change in Refractive Index with photon energy of CdS thin films.

D. Extinction Coefficient

The extinction coefficient allows for estimation of the molar concentration of a solution from its measured absorbance.

The extinction coefficient can be determined by using the relation, $k = \frac{\alpha\lambda}{4\pi}$, where λ is the wavelength of light.

Fig.7 shows the plot between photon energy Vs extinction coefficient. The extinction coefficient increases with increasing photon energy up to 2.8 eV then it becomes almost constant for bulk CdS thin film. It increases with photon energy up to 2.8eV then decreases slightly for nano thin film of CdS at room temperature. It again increases with photon energy. Nano thin film at 50°C initially decreases up to 2.3 eV then increases with photon energy from 2.3eV to 4eV, which shows that the absorbance coefficient increases or transmittance increases or

film thickness decreases because $\alpha = \log \frac{T}{t}$, t is the film thickness.

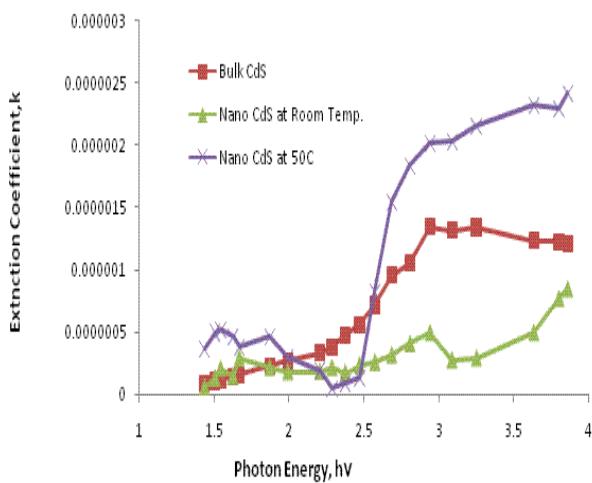


Fig.7 Change in Extinction Coefficient with photon energy of CdS thin films.

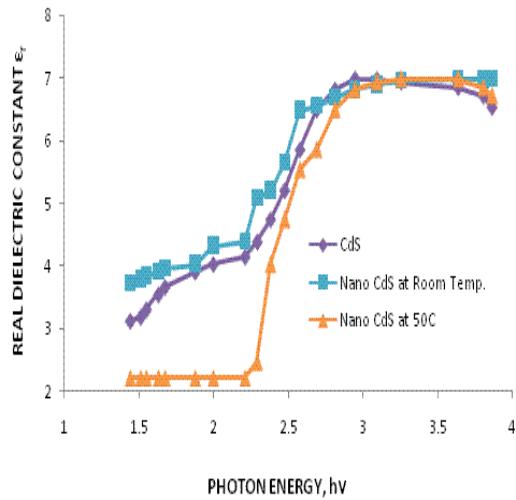


Fig.8. Plot between photon energy (hv) and Real Dielectric Constant.

E. Dielectric Constant

The dielectric constant and absorption coefficient are related and can be obtained theoretically with the relation given by the following: [Ugwu, 2006; Okujagu, 1992; Parachiniet et

al., 1980; Chalkwski, 1980; Born et al., 1970; and Jenkins et al., 1976].

$$\epsilon_r = n^2 - k^2 \text{ and } \epsilon_i = 2nk$$

Where (ϵ_r) the real part of the dielectric constant, (ϵ_i) is the imaginary part of the dielectric constant, (n) is the refractive index of the material and (k) is the extinction coefficient given by:

$$k = \frac{\alpha\lambda}{4\pi}$$

Where (α) is the absorption co-efficient and (λ) is the wavelength of the radiation.

Fig.8 shows a plot between photon energy and real dielectric constant

$$\epsilon_r = n^2 - k^2$$

The real part of the dielectric constant (shown in Fig.8) almost constant up to 2.24eV and increases slowly with photon energy 2.25eV then increases up to 2.8eV after that it again becomes constant up to 3.8eV.

The imaginary part of dielectric constant $\epsilon_i = 2nk$, represents the absorption associated of radiation by free carriers.

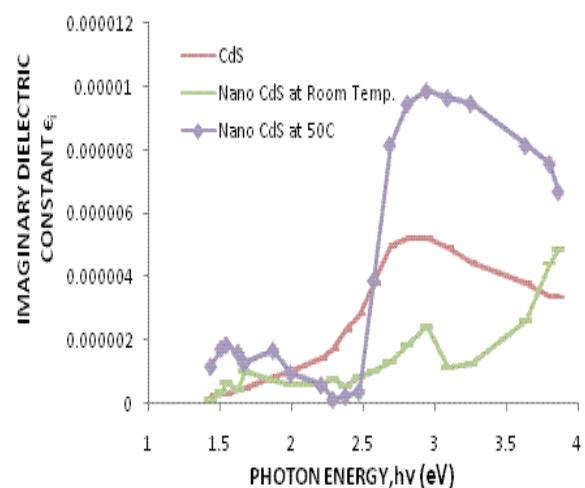


Fig.9. Plot between photon energy (hv) and Imaginary Dielectric Constant.

In metals imaginary part is always positive and represents loss factor or energy absorbed. The plot of imaginary part of dielectric constant as function of energy (shown in Fig.9) is initially increasing exponentially then decreases after 2.8eV to 4eV for bulk CdS thin film. The imaginary part of nano CdS at room temperature increases with increase in photon energy but the imaginary part of CdS initially decreases up to 2.5eV then increases exponentially up to 2.8eV then decrease slowly up to 4eV of photon energy. Imaginary part of dielectric constant is also related to conductivity so we can infer that energy lost to the metals appears as conductivity, but then it is directly proportional to conductivity but conductivity plots (as function of energy again) shows structures.

IV. CONCLUSIONS

This work has clearly presented how CdS thin films of bulk and nano material was grown using Chemical Bath Deposition techniques and how the effect of the solid state properties on spectral absorbance, transmission, and reflectance were obtained. The behavior of the film as illustrated in the graphs shows that the film is a visible transmitting thin film. The absorbance at the near infrared domain is low with high transmittance at the same region. The data explain the relationship between extinction coefficients, refractive index, real and imaginary dielectric constants and optical conductance.

ACKNOWLEDGEMENT

The authors are thankful to the Management, Bhilai Institute of Technology, Durg, (C.G.) for providing all the facilities in lab.

REFERENCES

- [1] R. Banerjee, R. Jayakrishnan, P Ayyub, J Physics Condens Matter 12, 10647 (2000).
- [2] G. Brusatin, M. Guglielmi, P. Innocenzi, A. Martucci, G. Scarinci, J. Electrocer. 151,4(2000)
- [3] M. Tamborra, M. Striccoli, R. Comparelli, M. L. Curri, A. Petrella and A. Agostiano, Nanotechnology 15, 5240(2004)
- [4] N. Tessler, V. Medvedev, M. Kazes, S. Kan and U. Banin, Science 295, 1506 (2002)
- [5] L. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hallingsworth and C A Leatherdale, Science 290, 340 (2000)
- [6] D Battaglia and X Peng, Nano Letter. 2, 1027 (2002)
- [7] M. Abdulkhadar and Binny Thomas, Nano Structured Material. 5, 289 (1995)
- [8] J. Nanda, K. S. Narayan, Beena Annie Kuruvilla, G. L. Murthy, D. D. Sharma, Applied Physics, 72, 11(1998).
- [9] L Brus, Applied Physics, A53, 465 (1991).
- [10] K. Nanda, S. N. Sarangi, S. N. Sahu, Nano Structured Material, 10, 1401(1998).
- [11] Z.Rizwan, B.Z Azmi, M.G.M. Sabri, optoelectronic and advanced materials 5, 4,(2011), 393-397.
- [12] Shikha Tiwari and Sanjay Tiwari, Crystal Research Technology, 41, 82,(2006).
- [13] P.Chouksey, B.P. Chandra, M. Rakhiyani, Indian J of Engg. And Material science 16,2009,157-160.
- [14] E.I.Ugwa.,D.U.Onah, The pacific journal of science and technology 8, 1, 2007, 155-161.
- [15] M. Y. Nadeem, W. Ahmed, Turk J. Phy, 24 ,651-659,(2000).